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June 01, 2004

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APPLICATION NUMBER: ***60/463,465***
FILING DATE: ***April 16, 2003***
RELATED PCT APPLICATION NUMBER: ***PCT/US04/11576***

By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS

N. WOODSON
Certifying Officer

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SUBMITTED OR TRANSMITTED IN COMPLIANCE WITH RULE 17.1(a) OR (b)

JC904 U.S. PTO
04/16/03

60463465 . 041603

ATTORNEY DOCKET NO. EER.P0017P

J1050 U.S. PTO
60/463465
04/16/03

IN THE U.S. PATENT AND TRADEMARK OFFICE
Provisional Application Cover Sheet

ASSISTANT COMMISSIONER FOR PATENTS
Washington, D.C. 20231

This is a request for filing a PROVISIONAL APPLICATION under 37 CFR 1.53 (b)(2).

INVENTOR(s)/APPLICANT(s)

Last Name	First Name, MI	Residence (City and Either State or Foreign Country)
Timpe	Ronald	Grand Forks, ND
Aulich	Ted	Grand Forks , ND

TITLE OF THE INVENTION

PROCESS FOR PRODUCING HIGH-PRESSURE HYDROGEN

CORRESPONDENCE ADDRESS

Customer Number 30163

30163
PATENT TRADEMARK OFFICE

ENCLOSED APPLICATION PARTS (check all that apply)

- ☑ Specification — *Number of Pages:* 6 *(including cover page)* — (X) Small Entity Status Claimed
- ☑ Drawing(s) — *Number of Pages:* 1 *(included with Specification)*
- ☐ Power of Attorney
- ☐ Additional inventors are being named on separately numbered sheets attached hereto.

METHOD OF PAYMENT

A PTO-2038 Credit Card Payment Form in the amount of $80.00 to cover the filing fee is enclosed.

Charge $_______ to Deposit Account ____________.

Respectfully submitted,

Bruce A. Johnson
Attorney for Applicant(s)
Reg. No. 37361

Date: 4-16-03

Telephone No.: 512-301-9900

"Express Mail" label no. EO 900 723 414 US

Date of Deposit: 4-16-03

I hereby certify that this is being deposited with the United States Postal Service 'Express Mail Post Office to Addressee' service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner for Patents, Box Provisional Application, Washington, D.C. 20231.

By ____________
Typed Name: Bruce A. Johnson

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PTO/SB/17 (09-00)
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FEE TRANSMITTAL for FY 2001

Patent fees are subject to annual revision.

Complete if Known	
Application Number	TBD
Filing Date	4/16/2003
First Named Inventor	Ronald Timpe
Examiner Name	
Group Art Unit	
Attorney Docket No.	EER.P0017P

TOTAL AMOUNT OF PAYMENT $80.00

METHOD OF PAYMENT

1. ☐ The Commissioner is hereby authorized to charge indicated fees and credit any overpayments to:

Deposit Account Number: ____

Deposit Account Name: ____

☐ Charge Any Additional Fee Required Under 37 CFR 1.16 and 1.17

☐ Applicant claims small entity status. See 37 CFR 1.27

☑ **Payment Enclosed:**

☐ Check ☑ Credit Card ☐ Money Order ☐ Other

FEE CALCULATION

1. BASIC FILING FEE

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description	Fee Paid
101	750	201	375	Utility filing fee	
106	330	206	165	Design filing fee	
107	490	207	245	Plant filing fee	
108	750	208	375	Reissue filing fee	
114	160	214	80	Provisional filing fee	$80

SUBTOTAL (1) $ 80.00

2. EXTRA CLAIM FEES

			Extra Claims		Fee from below		Fee Paid
Total Claims	0	-20**=	0	X	$18	=	$0.00
Independent Claims	0	-3**=	0	X	$84	=	$0.00
Multiple Dependent						=	

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description
103	18	203	9	Claims in excess of 20
102	84	202	42	Independent claims in excess of 3
104	270	204	135	Multiple dependent claim, if not paid
109	80	209	40	** Reissue independent claims over original patent
110	18	210	9	** Reissue claims in excess of 20 and over original patent

SUBTOTAL (2) $0.00

FEE CALCULATION (continued)

3. ADDITIONAL FEES

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description	Fee Paid
105	130	205	65	Surcharge - late filing fee or oath	$0
127	50	227	25	Surcharge - late provisional filing fee or cover sheet	$0
139	130	139	130	Non-English specification	$0
147	2,520	147	2,520	For filing a request for *ex parte* reexamination	$0
112	920*	112	920*	Requesting publication of SIR prior to Examiner action	$0
113	1,840*	113	1,840*	Requesting publication of SIR after Examiner action	$0
115	110	215	55	Extension for reply within first month	$0
116	390	216	195	Extension for reply within second month	$0
117	890	217	446	Extension for reply within third month	$0
118	1,390	218	695	Extension for reply within fourth month	$0
128	1,890	228	945	Extension for reply within fifth month	$0
119	310	219	155	Notice of Appeal	$0
120	310	220	155	Filing a brief in support of an appeal	$0
121	270	221	135	Request for oral hearing	$0
138	1,510	138	1,510	Petition to institute a public use proceeding	$0
140	110	240	55	Petition to revive – unavoidable	$0
141	1,240	241	620	Petition to revive – unintentional	$0
142	1,240	242	620	Utility issue fee (or reissue)	$0
143	440	243	220	Design issue fee	$0
144	600	244	300	Plant issue fee	$0
122	130	122	130	Petitions to the Commissioner	$0
123	50	123	50	Petitions related to provisional applications	$0
126	240	126	240	Submission of Information Disclosure Stmt	$0
581	40	581	40	Recording each patent assignment per property (times number of properties)	$0
146	710	246	355	Filing a submission after final rejection (37 CFR § 1.129(a))	$0
149	710	249	355	For each additional invention to be examined (37 CFR § 1.129(b))	$0
179	710	279	355	Request for Continued Examination (RCE)	$0
169	900	169	900	Request for expedited examination of a design application	$0

Other fee (specify) ____ $0

* Reduced by Basic Filing Fee Paid SUBTOTAL (3) $0.00

SUBMITTED BY				Complete (*if applicable*)	
Name (Print/Type)	Bruce A. Johnson	*Registration No. (Attorney/Agent)*	37361	*Telephone*	512-301-9900
Signature				*Date*	4/16/03

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PTO/SB/35 (11-00)
Approved for use through 10/31/2002. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

NONPUBLICATION REQUEST UNDER 35 U.S.C. 122(b)(2)(B)(i)

First Inventor	Ronald Timpe
Title	PROCESS FOR PRODUCING HIGH-PRESSURE HYDROGEN
Attorney Docket No.	EER.P0017P

I hereby certify that the invention disclosed in the attached application has not and will not be the subject of an application filed in another country, or under a multilateral agreement, that requires publication at eighteen months after filing.

I hereby request that the attached application not be published under 35 U.S.C. 122(b).

April 16, 2003
Date

Signature

Bruce A. Johnson
Name

This request must be signed in compliance with 37 CFR 1.33(b) and submitted with the application upon filing.

Applicant may rescind this nonpublication request at any time. If applicant rescinds a request that an application not be published under 35 U.S.C. 122(b), the application will be scheduled for publication at eighteen months from the earliest claimed filing date for which a benefit is claimed.

If applicant subsequently files an application directed to the invention disclosed in the attached application in another country, or under a multilateral international agreement, that requires publication of applications eighteen months after filing, the applicant must notify the United States Patent and Trademark Office of such filing within forty-five (45) days after the date of the filing of such foreign or international application. **Failure to do so will result in abandonment of this application (35 U.S.C. 122(b)(2)(B)(iii)).**

United States Provisional Patent Application for

PROCESS FOR PRODUCING HIGH-PRESSURE HYDROGEN

Inventors:
Ronald Timpe
Ted Aulich

Field of Invention

The present invention is a process for producing high-pressure hydrogen from natural gas, methanol, ethanol, and other fossil fuel-derived and renewable hydrocarbon resources. The process can produce hydrogen at pressures ranging from 500 to 10,000 pounds per square inch (psi) using 1) a hydrocarbon-based hydrogen carrier; 2) "supercritical" water, which refers to water maintained at or above its supercritical temperature and pressure requirements of at least 375°C and 3200 psi, respectively; and 3) an appropriate catalyst. In work performed using either natural gas (methane) or methanol as hydrogen carrier, the process yielded gaseous products with hydrogen concentrations of up to 19 mole percent (mol%) and 66 mol%, respectively, neither of which are meant to be the limit expected under optimal conditions. With methanol as hydrogen source, nonhydrogen product gas constituents included carbon dioxide, carbon monoxide, methane, ethane, and nitrogen. With methane as hydrogen source, nonhydrogen product gas constituents included methane, nitrogen, oxygen, ethane, and no detectable carbon monoxide.

One application of the process is for on-demand production of high-pressure hydrogen for fuel cells, including proton exchange membrane (PEM) fuel cells used for powering transportation vehicles, and PEM and other fuel cells used for other mobile and stationary power production purposes. Utilizing the process for PEM fuel cell applications may require integration with a hydrogen purification technology, since PEM fuel cells require low-contaminant-level hydrogen for trouble-free operation and maximum power density. Upon successful integration with a hydrogen purification technology, the process will hold two significant advantages over other technologies being pursued for producing hydrogen for fuel cell vehicles: 1) elimination of the need for expensive hydrogen compression and 2) significant reduction of the need for expensive storage of high-pressure hydrogen.

Problem, Background, and Theory

A key challenge to transitioning the U.S. transportation economy from the gasoline- and diesel-powered internal combustion engine to the hydrogen-powered fuel cell is lack of an economically viable means of supplying fuel cell-quality hydrogen. Two basic hydrogen supply options are on-board-vehicle extraction of hydrogen from hydrocarbon fuels or on-board-vehicle storage of hydrogen produced and dispensed at a stationary facility. Within these two basic options, numerous specific variations are being studied and/or developed, including, but not limited to 1) on-board-vehicle extraction of hydrogen from gasoline, diesel fuel, naphtha, and

methanol; 2) fuel station site hydrogen production via steam methane (natural gas) reforming (SMR) or other hydrocarbon-based processes; 3) fuel station site hydrogen production via electrolysis of water; 4) centrally produced (via large-scale SMR, electrolysis, and other processes) hydrogen delivered to a fuel station by truck or pipeline; and 5) other supply scenarios involving hydrogen production via photochemical, gasification, nuclear, biomass-based, biological, and solar-, wind-, and hydro-powered methods.

Today, SMR is the most common and least expensive method of hydrogen production, accounting for about 95% of the hydrogen produced in the United States. In SMR, methane is reacted with steam to produce a mixture of hydrogen, carbon dioxide, carbon monoxide, and water, and the mixture is separated to yield high-purity hydrogen. Because of its status as a mature, reliable, economically viable technology, major industrial companies are developing hydrogen vehicle refueling station concepts based on the use of on-site SMR, which involves scaling the process down significantly from its most common commercial application of producing hydrogen at petroleum refineries for use in making cleaner-burning gasoline. Key challenges associated with on-site hydrogen generation derive from the unpredictable demands of vehicle fueling. Because SMR works best at steady-state, 24-hours-per-day, full-capacity operation, integration with a hydrogen fuel station will require on-site hydrogen compression and storage—as a gas, a liquid, or in a chemical compound—to compensate for fluctuating hydrogen demand. Because of its small molecular size, hydrogen is much more difficult and expensive to compress than natural gas, and none of the hydrogen storage technologies available today represent an ideal combination of economy, performance, durability, and safety. The present invention offers a means to produce high-pressure hydrogen, thereby eliminating the need for expensive hydrogen compression. In addition, the present invention will be compatible with on-demand production of high-pressure hydrogen, which will translate to a greatly diminished hydrogen storage volume requirement versus SMR and other demand-unresponsive processes.

General Description

The present invention is similar to SMR in that both processes involve the use of natural gas as a hydrogen carrier, water as a reactant, and a catalyst to promote methane reforming to hydrogen and carbon dioxide. Two key differences between the two processes are the temperature and pressure ranges utilized in the reforming reaction. In the present invention, the reactor is maintained within temperature and pressure ranges of 375°–600°C and 3200–10,000 psi, respectively, whereas SMR utilizes reaction temperatures and pressures ranging from about 700°–950°C and 300–600 psi, respectively. A third key difference is that the present invention can be utilized with hydrogen carriers other than natural gas/methane, including—but not limited to—propane, butane, methanol, and ethanol. Figure 1 is a schematic diagram of a reactor system utilized in developing the present invention. As outlined in Figure 1, the reactor system can be configured to extract hydrogen from a liquid or gaseous, water-soluble or water-insoluble hydrogen carrier.

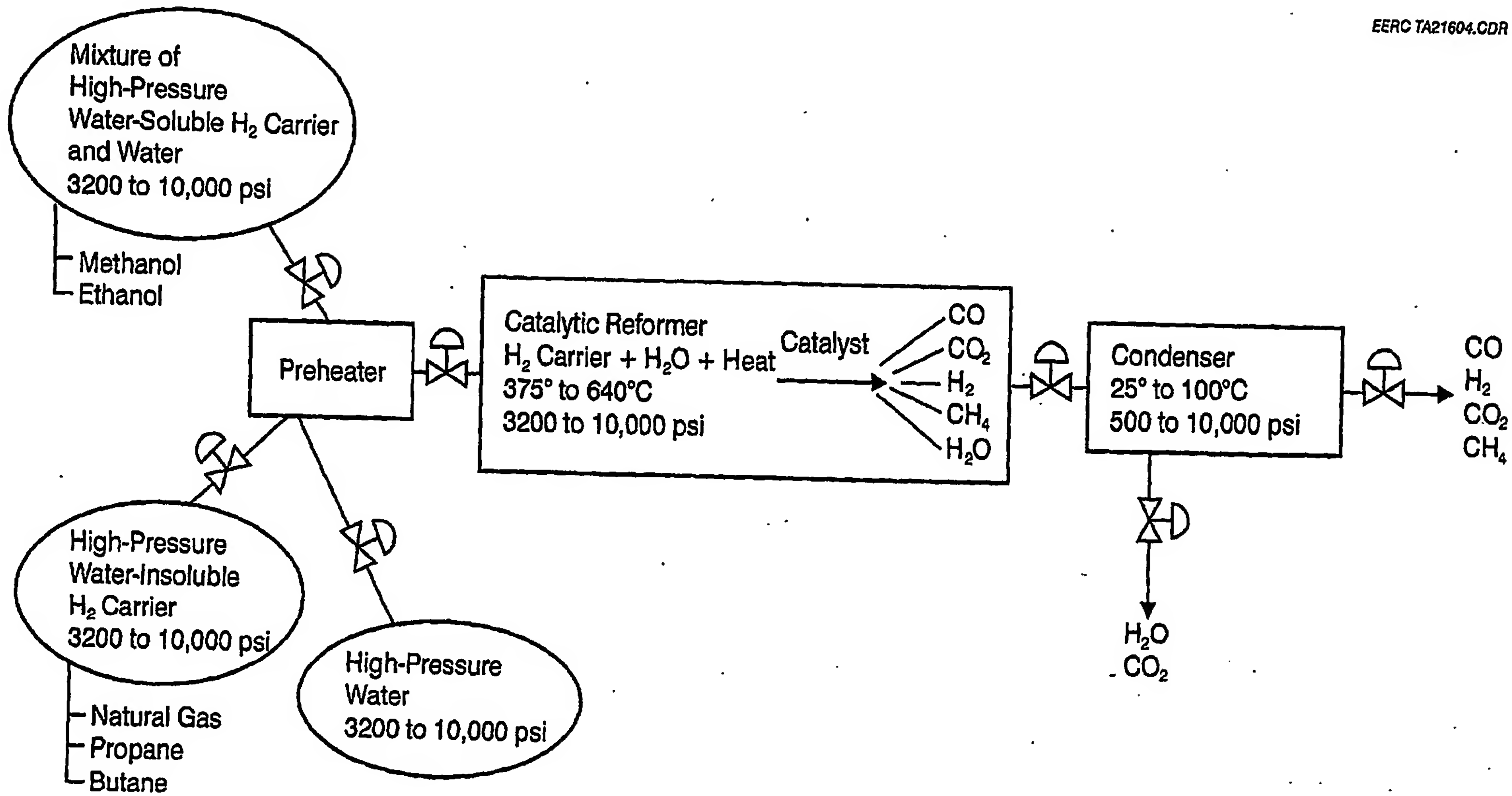

Figure 1. Process for production of high-pressure hydrogen.

In utilizing natural gas or another water-insoluble hydrogen carrier, high-pressure water and natural gas are separately injected into the preheater at an appropriate water-to-hydrogen carrier molar ratio. Tests conducted to date have utilized water-to-hydrogen carrier molar ratios ranging from 0.5:1 to 4:1. In general, for water-based reforming of any hydrogen carrier, utilization of a water-to-hydrogen carrier molar ratio of at least 1:1 ensures availability of sufficient oxygen to guard against undesired carbon build-up on catalyst used to promote the reforming reaction. However, minimal usage of supercritical water is desired to minimize process energy input, and lower water-to-hydrogen carrier molar ratios may be achievable with improved reforming catalysts. Following mixing and heating in the preheater, the reactant mixture flows into the reformer, which comprises a tubular reactor containing a commercially available reforming catalyst. The process is compatible with continuous-flow operation, and residence time in the reformer is a function of pressure and flow rate through the reformer.

Reformate products exit the reformer and flow into the condenser, in which water and a portion of the carbon dioxide product are condensed. Pressure in the condenser and pressure of the product gas stream exiting the condenser can be maintained at or near pressure in the reformer (or lower, if desired) by adjustment of the control valve at the condenser exit. In utilizing methanol or another water-soluble hydrogen carrier, a mixture of methanol and water is pressurized and injected into the preheater at an appropriate water-to-hydrogen carrier molar ratio. From the preheater on downstream through the reactor system, process steps and conditions are identical to those utilized for natural gas.

Specific Example: Hydrogen Production from Natural Gas

Table 1 presents compositional data on four different product gas samples collected during a series of tests utilizing natural gas/methane as hydrogen carrier. All tests employed an approximate 4:1 water-to-methane molar ratio and a reformer temperature and pressure of about 440°C and 3500 psi, respectively. The first column of data is for a sample collected from a continuous-process test in which residence time in the reformer was about 2 seconds. The three remaining data sets are for tests in which reformer residence time was increased by operating the reactor system in batch mode, with the objective of investigating the effect of residence time on product gas composition. Estimated residence time for Batch 1–3 tests was about 3, 10, and 15 minutes, respectively. The batch test results indicate that—under the conditions evaluated—residence time has no effect on product gas composition. Of primary significance in the natural gas results is the consistent absence of carbon monoxide in the product gas. With the gas chromatography-based analytical procedure employed for product gas characterization, the detection limit for carbon monoxide is about 100 parts per million (ppm), which means that if carbon monoxide is present in the product gas, it is present at a concentration of below 100 ppm. Carbon monoxide is one of two contaminants of major concern regarding hydrogen for PEM fuel cell applications (the other being sulfur species), which means that its absence from the product gas stream represents a significant process advantage.

Table 1 – High-Pressure Hydrogen from Natural Gas—Product Gas Composition

Sample	Continuous 1	Batch 1	Batch 2	Batch 3
Hydrogen, mol%	19.3	19.9	16.9	16.4
Carbon Dioxide, mol%	7.6	8.6	5.1	6.3
Methane, mol%	72.6	70.1	76.6	75.7
Ethane, mol%	0.4	1.1	1.2	1.4
Propane, mol%	0.0	0.3	0.0	0.1
cis-2-Butene, mol%	0.0	0.0	0.0	0.0
Carbon Monoxide, mol%*	0.0	0.0	0.0	0.0

* Analytical detection limit for carbon monoxide was 100 ppm.

Specific Example: Hydrogen Production from Methanol

Table 2 presents compositional data on four different product gas samples collected during a series of tests utilizing methanol as hydrogen carrier. All tests employed an approximate 1:1 water-to-methanol molar ratio and a reformer temperature and pressure of about 380°C and 3200 psi, respectively. The first two data columns are for samples collected from continuous-process tests in which residence time in the reformer was about 2 seconds. The two remaining data sets are for tests in which reformer residence time was increased by operating the reactor system in batch mode, with the objective of investigating the effect of residence time on product gas composition. Estimated residence time for Batch 1 and 2 tests was about 3 to 5 minutes. The batch test results indicate that—under the conditions evaluated—residence time has a measurable effect on product gas composition, most significantly on level of hydrogen and carbon dioxide.

Table 2 – High-Pressure Hydrogen from Methanol—Product Gas Composition

Sample	Continuous 1	Continuous 2	Batch 1	Batch 2
Hydrogen, mol%	65.1	66.4	72.4	69.7
Carbon Dioxide, mol%	23.9	23.8	16.8	17.1
Methane, mol%	6.5	5.4	4.9	7.6
Ethane, mol%	0.1	0.1	0.1	0.0
Propane, mol%	0.0	0.0	0.0	0.0
cis-2-Butene, mol%	0.1	0.1	0.5	0.4
Carbon Monoxide, mol%	4.3	4.2	5.4	5.2

Outline of the Invention

This invention is a method for the production of high-pressure hydrogen for use in PEM and other fuel cell applications. An example of the invention includes the steps of:

1) Injection of supercritical water and high-pressure water-soluble or water-insoluble hydrogen carrier into a catalytic reformer, using the following exemplary materials, proportions, and reaction conditions:
    a) Hydrogen carrier – natural gas, propane, butane, methanol, ethanol, or other.
    b) Water–hydrogen carrier molar ratio – 0.1:1 to 4:1
    c) Reforming reaction temperature – 375° to 640°C
    d) Reforming reaction pressure – 3200 to 10,000 psi
    e) Residence time in reformer – 0.5 to 360 seconds
2) Generation of hydrogen, carbon dioxide, and other reformate gas species.
3) Condensation to remove water and a portion of carbon dioxide.
4) Recovery of high-pressure hydrogen and other reformate gas species.

Following is an outline of various examples of features of the invention. Note that other techniques and embodiments are also possible within the spirit and scope of the invention.

A) Materials, Proportions, and Reaction Conditions that Demonstrated Desired Results
    1) Natural gas as hydrogen carrier
        a) Water–methane molar ratio – 4:1
        b) Reforming reaction temperature – 440°C
        c) Reforming reaction pressure – 3500 psi
        d) Residence time in reformer – about 2 seconds
    2) Methanol as hydrogen carrier
        a) Water–methanol molar ratio – 1:1
        b) Reforming reaction temperature – 380°C
        c) Reforming reaction pressure – 3200 psi
        d) Residence time in reformer – about 2 seconds

B) Other Hydrogen Carriers to Which Invention May Be Applied (Partial List)
    1) Propane
    2) Butane
    3) Ethanol
    4) Naphtha
    5) Ammonia